Europäisches Patentamt
European Patent Office
Office européen des brevets

Publication number: 0 201 331
A2

EUROPEAN PATENT APPLICATION

Application number: 86303487.2

Date of filing: 08.05.86

Int. Cl.: B 29 C 61/00, C 08 J ..., C 08 L 23/06, C 08 L 23/... // B29K23:00, B32B ..., B32B31:30

Priority: 08.05.85 US 732127

Date of publication of application: 12.11.86 Bulletin 86/46

Designated Contracting States: BE DE FR GB IT NL SE

Applicant: EXXON CHEMICAL PATENTS INC., 200 Park Avenue, Florham Park New Jersey 07932 (US)

Inventor: Hodgson, William John, Jr. ... Southwood, Baytown Texas 77520 (US)
Inventor: Middlesworth, Jeffrey Alan, 453 Lost Rock Drive, Webster Texas 77589 (US)

Representative: Northover, Robert Frank et al, ESSO Chemical Limited Esso Chemical Research Centre P.O. Box 1, Abingdon Oxfordshire, OX13 6BB (GB)

Oriented elastomeric film and method of manufacture.

An oriented thermoplastic elastomer comprising an elastomer, EVA and process oil is prepared by stretch orienting the film at an elevated temperature and annealing the film to freeze in stresses and strains in the film. In one embodiment, the thermoplastic elastomer is provided with a thin coating of a thermoplastic to provide nonblocking.

EP 0 201 331 A2

Oriented Elastomeric Film and Method of Manufacture

This invention relates generally to the thermoplastic elastomers and in particular, to the thermoplastic elastomers which have been thermally oriented.

Thermoplastic elastomers possess properties of both thermoplastics and elastomers and have a wide range of applications. In certain applications, a thermoplastic elastomer film is dimensionally stabilized in a stretched condition (wherein stresses and strains in the film have been frozen in) for subsequent use. For example, the stretched thermoplastic elastomer may be applied to a substrate and later heated causing the thermoplastic elastomer to shrink and retain substantial elastic properties. One such use is disclosed in European Patent Application No. 84301717.9 (Publication Number 0119...) wherein the stretched dimensionally stable thermoplastic elastomer is placed on a diaper waistband and reheated causing the thermoplastic elastomer to contract and revert to a heat stable elastic state. The diaper thus, is provided with a flexible and stretchable waistband. A similar application of thermoplastic elastomers is disclosed in European Patent Application No. 84301720.38(Publication Number 0119827). These publications are cited merely to disclose a possible use of thermoplastic elastomers.

In many applications, particularly where the thermoplastic elastomer is secured to a substrate for later contraction by the application of heat, it is important that the thermoplastic elastomer have relatively high shrink force since the substrate resists shrinkage. The shrink force is determined by measuring the shrinkage of the film sample against an applied force and is referred to herein as weighted shrink. The weighted shrink properties differ markedly from free shrinkage (no applied weight) and hence is a key property in determining the suitability of a heat shrinkable film on substrates.

U.S. Patent 4,303,571, issued to D. S. Jansen et al disclose a thermoplastic elastomer film comprising 25 to 55 parts by weight of an ethylene-propylene copolymer, 35 to 55 parts by weight of an EVA copolymer and 15 to 25 parts by weight of a liquid hydrocarbon process oil.

As will be demonstrated in the discussion [illegible] examples contained herein, the elastomeric fi[illegible] tion disclosed in U.S. Patent No. 4,303,571 [illegible] shrink properties, but not nearly as good as [illegible] composition of the present invention, particularly [illegible] weighted shrink properties.

A problem associated with thermoplastic [illegible] ness which impedes unwinding of the film during process[illegible] particularly serious problem with film composi[illegible] processing oil. Moreover, addition of particulat[illegible] particularly effective in thermoplastic elast[illegible] difficulty in dispersing the additives uniform[illegible] since the additives tend to concentrate in th[illegible] phase.

SUMMARY OF THE INVENTION

The present invention provides an [illegible] film composition and process for manufacturing which exhibits excellent shrink force and possesses nonblocking properties.

The film composition in one embodiment of the present invention comprises from 10 to 40 weight percent of an olefinic elastomer, not more than 12 weight percent (preferably not more than 10 weight percent) of a normal liquid processing oil, and from 50 to 80 weight percent of a thermoplastic ethylene copolymer, preferably vinyl acetate copolymer (EVA), all weight percents based on the weight of the three component composition. The film is dimensionally stable in a stretched condition (draw ratio of 1.3:1 to 6:1) and is contractible to a thermally stable and elastic condition by the application of heat.

The method for preparing the thermoplastic elastomer film comprises stretching the film at a temperature below the melting point of the EVA component at a draw ratio between about 1.3:1 and 6:1, annealing the stretched film, and cooling of the film to ambient temperature. The film may be used by securing it to a substrate such as a inelastic thermoplastic or fabric, and heating the film to an elevated temperature whereby the film contracts to a thermally stable length and possesses elastic properties. The composite thus may be expanded by the application of tension which upon release returns to its original shape.

In another embodiment of the invention, the film comprises a composite of one layer of a thermoplastic elastomer and a thin coating of an ethylene polymer or copolymer having a relatively high Melt Index. Upon the subsequent stretch orienting the composite, the coating becomes even thinner. The thermoplastic elastomer layer is preferably the composition as defined above, particularly if [illegible] shrink force is desired in addition to antiblock properties. The coating preferably also contains particulate antiblock additives, thus avoiding the difficult problem of distributing antiblock particles in or near the film surface.

The present invention contemplates (1) an improved [illegible] oriented, dimensionally stable thermoplastic elastomer film which is shrinkable upon application of heat, (2) a composite of a thermo-plastic elastomer and a substrate wherein the orientation has been released by the application of heat, (3) a method of preparing the oriented thermoplastic elastomer film, (4)- a method of manufacturing an elastic composite comprising a thermoplastic elastomer and a sub-strate of inelastic material, (5) a thermoplastic elastomer having a thin coating of a nonblocking polymer and (6) a method of preparing a nonblocking thermoplastic elastomer.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In describing the present invention, it is necessary to use certain technical terms, some of which are commonly used in the industry and others of which are defined herein to express a concept.

In order to avoid confusion, the following terms used herein shall have the meaning indicated:

"Draw ratio" - the ratio of the final stabilized length (after orientation and "snapback") of an oriented film and the initial length of the film before orientation. Draw ratio in unidirectional orientation is also equal to the ratio of the thickness of the stabilized oriented film and the initial unoriented film.

"Shrink force" - the force required to prevent shrinkage of an oriented film by application of heat.

"Shrink stress" - the shrink force per unit area (g/cm^2).

"Annealing" - a heat treatment process for reducing [illegible] and stresses set up in the film during orientation. The process comprises maintaining the film while in [illegible]

condition at the annealing temperature, for [illegible] followed by cooling the film to room temp[illegible]

"Thermoplastic elastomer" - frequently call[illegible] plastics, are blends of a thermoplastic [illegible] mer that are processable as a melt, at [illegible] but exhibit properties similar to [illegible] room temperature.

"Melt Index" (MI) - g/10 min (ASTM-D [illegible]

In its broadest form, the thermoplastic [illegible] sition of the present invention comprises thr[illegible] (1) olefinic elastomer, (2) ethylene copolymer [illegible] process oil.

The concentrations of the three compon[illegible] are as follows:

Component	Concentration	Preferred Concentration	Most Preferred
Olefinic Elastomer	10-40 wt %	15-3[illegible] wt %	[illegible]-30 wt %
Ethylene Copolymer	50-80 wt %	60-80 wt %	[illegible] wt %
Process Oil	0-12 wt %	2-10 wt %	[illegible] wt %

The above concentration range may be combined in any permissible combination, although the particular combinations shown are preferred. For example, a preferred composition comprises 10-40 wt % elastomer, 60-80 wt % ethylene copolymer, and 0-12 wt % process oil. The weight concentration of each component is based on the total weight of the three main components.

Elastomer Component: The olefinic elastomer component of the composition preferably comprises an ethylene copolymer elastomer, such as a copolymer of ethylene with higher alpha-olefin. Preferred ethylene elastomer copolymers include EPM (ASTM D-1418-72a designation for an ethylene-propylene elastomer copolymer) or EPDM (ASTM D-1418-72a designation for an ethylene-propylene diene elastomer terpolymer). Also usable are high molecular weight polyisobutylene, butyl rubbers and halogenated butyl rubbers.

Preferred ethylene elastomer copolymers for [illegible] comprise from 30 to 90 weight percent ethylene, more preferably from 35 to 80 weight percent ethylene, and most preferably from 50 to 80 weight percent ethylene and have a Mooney viscosity (ML 1+8 at 127° C) between 25 and 80.

EPDM is a terpolymer of ethylene, a higher alpha-olefin such as propylene, and a nonconjugated diene. In such elastomers the nonconjugated diolefin may be straight chain, branched chain or cyclic hydrocarbon diolefins having from 6 to 15 carbon atoms.

Of the nonconjugated dienes typically used in these copolymers, preferred are dicyclopentadiene, 1,4-hexadiene, 5-methylene-2-norbornene and 5-ethylidene-2-norbornene; 5-ethylidene-2-norbornene (ENB) and 1,4-hexadiene are particularly preferred diolefins. EPDM elastomers and their method of manufacture are well known to those skilled in the art. Oil extended EPDM elastomers may also be used. Preferred EPDM elastomers contain from 30 to 90 weight percent ethylene and most preferably from 50 to 80 weight percent ethylene, and from 0.5 to 15 weight percent of the nonconjugated diolefin.

As mentioned above, the olefinic elastomer useful in this invention may also be a polyisobutylene, a copolymer of isobutylene and isoprene (generally known as butyl rubber) or a halogenated copolymer of isobutylene and isoprene (generally known as halogenated butyl rubber, such as chlorinated, brominated and chlorobrominated butyl rubber). Butyl rubber is a vulcanizable rubber copolymer containing from 85 to 99.5 percent combined isoolefin having from 4 to 8 carbon atoms and from 0.5 to 15 percent combined conjugated diolefin having from 4 to 8 carbon atoms. Such copolymers and their preparation are well known, and generally the isoolefin is a compound such as isobutylene and the diolefin is a compound such as butadiene or isoprene. Halogenated butyl rubbers are also well known; chlorinated and brominated butyl rubber generally contains from 1.0 to [illegible] weight percent bromine and from 0.05 to 0.5 weight percent chlorine.

<u>Ethylene Copolymer Component:</u> The ethylene copolymers include those of ethylene and alpha-olefins having 3 to 16 carbon atoms such as propylene or 1-butene. Also included are copolymers of ethylene with unsaturated esters of a lower carboxylic acid or with an unsaturated carboxylic acid. In particular, copolymers of ethylene with vinyl acetate (EVA), or with acrylic acid (EAA), or methacrylic acid (EMA), are preferred. The ethylene copolymers to be used will generally contain from 50 to 99 weight percent ethylene, more preferably from 60 to 95 weight percent ethylene.

The most preferred ethylene copolymer [illegible] invention is EVA. The EVA may have a vinyl [illegible] between about 9% and 40% by weight, with [illegible] VA being preferred.

VA contents below about 9 wt % [illegible] flexibility and orientability for purposes [illegible] and VA contents above 40 wt % exhibit excess[illegible] balance of orientability and non tackiness [illegible] between 15 and 35 wt %.

Preferred Melt Index (ASTM-D-1238, [illegible]) from 1 to 20, with 2 to 10 being most preferred.

The ethylene copolymer component nor[illegible] operating temperatures of the tentering and [illegible] operations. [illegible] operations may be carried out at temp[illegible] [illegible]°F and below (preferably not more than 5.6°[illegible] [illegible] crystalline melting point of the ethylene copolymer compon[illegible] preferably is at ± 11.1°C of the orienting temp[illegible] [illegible] melting point of EVA ranges from approximately [illegible], depending on the VA content and MI, with the preferred [illegible] crystalline melting points between about 54°C and 71°C. For economics, orienting temperatures of 71°C and below are preferred.

<u>Process Oil Component:</u> Hydrocarbon oils useful in the present invention function as process aids whose activity is enhanced in the presence of vinyl acetate copolymers, as plasticizers producing low modulus and enhanced elasticity in the solid state and [illegible] useful are the normally liquid hydrocarbon processing and extender oils (ASTM D 2226) categorized as aromatic, highly aromatic, naphthenic and paraffinic process oils of a medium viscosity range. Oils sold under the trademarks "Flexon" and "Sunpar" have been found especially useful.

<u>Other Additives:</u> The composition may also include a filler material, an antiblock agent, processing aids, stabilizers and other conventional additives.

<u>FILM PREPARATION</u>

<u>Resin/Blend Preparation:</u> Preparation of compositions usable in this invention can be achieved in several different ways. The various components may be brought into intimate contact [illegible] example, dry blending these materials and then [illegible] [illegible]

composition through a compounding extruder. Alternatively, [illegible] ponents may be fed directly to a mixing device such as a compounding extruder, high shear continuous mixer, two roll mill or [illegible] mixer such as a Banbury mixer. The optional ingredients [illegible] described can be added to the composition during this mixing [illegible]tion. Overall, the objective is to obtain a uniform dispersion [illegible] ingredients and this is readily achieved by inducing sufficient [illegible] and heat to cause the plastics component(s) to melt. However, [illegible] and temperature of mixing should be controlled as is normally [illegible] one skilled in the art so as to avoid molecular weight degradation.

<u>Film Extrusion:</u> Film from the resin compound may be manufactured by conventional tubular extrusion, (blown bubble process) or [illegible] cast extrusion, with the latter being preferred. In [illegible] extrusion process, the molten resin is extruded from an elongated die [illegible] form of a web. The web is cast onto a chill roller, which solidifies the polymer, and finally wound into a roll.

The extrusion temperatures, die temperatures, and chill roll temperatures will depend on the composition employed, but generally will be in the following ranges for the compositions of the present invention prepared by cast extrusion:

Melt Temperature (°F)	350-450	(°C) [illegible]
Die Temperature (°F)	350-450	(°C) [illegible]
Chill Roll Temperature (°F)	70-130	(°C) [illegible]

The process described above may also include a set of embossing rolls to chill and form the film.

<u>Orientation:</u> Orientation of the film may be carried out in the machine direction (MD) or the transverse direction (TD) or both directions (biaxially) using conventional equipment and processes.

For orientation in the MD, a polymeric film [illegible] temperature (but below the crystalline melting point of [illegible]) is passed from a feed roll of film around two rollers [illegible] ferent surface speeds and finally to a takeup roller. [illegible] roller closest to the takeup roll is driven faster than the [illegible] roller closest to the feed roll, such that the film is stretched between the driven rollers. The assembly may include a roller inter[illegible]mediate the second roller and takeup roller to cool the film. The second roller and the takeup roller may be driven at the same [illegible]

pheral speeds to maintain the film in the stretched [illegible] supplementary cooling is not used, the film will [illegible] temperature on the take up roll.

The degree of stretch will depend upon the [illegible] pheral speeds of the driven rollers and the distance [illegible] the rollers. Stretch rates of 50 to 500 percent/minute will [illegible] factory for most MD orientation applications.

Preferably, however, film orientation will be carried out in a tentering device to impart TD orientation to the film. The film is cast as described above or is unwound from a film roll and then gripped by the edges for processing through the orientation steps. The film is passed successively through a preheat step, a stretching step at elevated temperatures (e.g. from 37.7° [illegible] a temperature slightly below the crystalline melting point of the ethylene copolymer), an annealing step, and finally a cooling step. (Although cooling may be considered part of the annealing step, for convenience it is described as a separate step herein.) The preheat, orientation, and a portion of the annealing temperature is controlled at an elevated temperature but below the crystalline melting point of the polymer. Although not essential, it is preferred that tension be maintained on the film during the annealing and cooling steps to minimize shrinkback. Upon cooling to ambient temperature (i.e., room temperature) or near ambient, the holding force may be released. The film may contract somewhat (snapback) in the TD but will retain substantial portion of its stretched length.

The tenter operating conditions can vary within relatively wide ranges and will depend on the several variables including film composition, film thickness, degree of orientation desired, annealing conditions, etc. The following is exemplary of a process for stretching 100 micron thick film (containing EVA) from 61 cm wide to a final width of about 152 cm, using a tenter manufactured by Marshall and Williams Company of Providence, Rhode Island.

ESTIMATED FILM RANGE

Step	Broad	Preferred	Typical
Preheat	100-160°F 37.7-71°C	115-140°F 46-60°C	125°F 51.6°C
Stretching	100-160°F 37.7-71°C	115-140°F 46-60°C	125°F 51.6°C
Annealing	100-150°F 37.7-71°C	110-150°F 43-66°C	120°F [illegible]
Cooling	Ambient	Ambient	Ambient

As indicated earlier, it is highly desirable to employ an annealing step in the process. Annealing partially relieves the internal stress in the stretched film and dimensionally stabilizes the film for storage. It has been found that by annealing the [illegible] temperature of ± 22.2°C, preferably ± 11.1°C of the orientation temperature (but slightly below the crystalline melting point of the ethylene copolymer) eliminates undesirable shrinkage during storage. The preferred annealing temperature is between 110°F and 130°F. Temperatures which result in excessive stress relieving should be avoided, since substantial frozen in stresses and strains should remain after the process is completed.

Annealing can be accomplished by maintaining the film in the stretched condition at the annealing temperature. Preferably, however, the annealing and cooling is carried out while permitting the film to contract slightly, but still under stress. The guide rails of the tenter can be arranged in a converging manner to provide the annealing and cooling while the film contracts. The controlled shrinkback of from 5 to 30%, preferably between 15 and 25%, of the maximum stretched width has given particularly good results in eliminating storage shrinkage. This annealing and preshrinking removes [illegible] the film stresses and strains so that shrinkage will not [illegible] storage temperature. However, the annealing and cooling [illegible] remove all the frozen in stress, and strain, since upon heating to elevated temperatures above storage temperature the film will shrink.

The degree of stretching may vary within wide ranges. Draw ratios of 1.3:1 to 6:1 are possible with 2:1 to 4:1 being preferred for TD tentering. The actual stretching will occur at higher ratios (1:5 to 9:1) to allow for controlled shrinkage and snapback.

EXAMPLES

In order to demonstrate the effectiveness of the present invention, particularly in respect of improved shrink force and non-blocking properties, a series of experiments were conducted [illegible] the performance of the film of the present invention with the prior art (U.S. Patent No. 4,303,571).

Film Samples:

Samples having the compositions listed in Table I were prepared by blending the components in the weight percentages indicated using a Banbury mixer. Each composition also included 6 wt % ethylene acrylic acid copolymer and filler material ($CaCO_3$). The resin blend was cast extruded into 150 micron (approx.) thick film using 7.6 cm extruder and 76.2 cm wide flat die.

Properties of the Film:

Each film sample was then tested for orientation/shrinkage properties with an Instron (Model 1122) in a temperature controlled chamber. 2.5 cm wide strips (cut in the TD) were taken from each sample, marked with lines 4 cm apart and then drawn to 9 cm at 10 cm/minute at an elevated temperature (60°C and 63°C). After orientation, each stretched film was quenched with water and removed from the Instron. Six film strips were drawn for each formulation and the test was run in random order in blocks of nine to eliminate systematic test error.

For each formulation, 6 strips were heated in the oven for three minutes at 65.5°C; three strips with a fixed weight and the other three strips freely suspended. The film strips were removed from the oven, allowed to cool and then measured to determine the % recovery.

The % recovery was calculated by the following formula:

$$\text{Percent Recovery} = \frac{\text{Initial length*} - \text{Final length**}}{\text{Initial length*} - 4\ \text{cm}} \times 100$$

* Initial stretched length (cm) after "snapback".

** Final length (cm) after full shrinkage at 150°F in oven.

Table II presents the results, comparing the three sample average for each formulation of the present invention (Samples A, B and C) with the three sample average of each formulation of the prior art (Samples D, E and F).

As revealed in Table II, the percent recovery under [illegible] strained conditions Samples A, B and C was higher than that of Samples D, E, and F. Percent restrained recovery for the A, B, C sample group averaged 85.4%, whereas that of D, E F group averaged [illegible]. [illegible] shrink force, which is the force required to keep the [illegible] shrinking can be calculated from these data. As [illegible] the shrink force for Samples A, B and C was substantially [illegible] that for Samples D, E, and F. Samples A and B exhibited particularly improved shrink force.

The higher shrink force of the Samples A, B and C permits the [illegible] of a thinner gauge film at the same draw ratio as demonstrated by the following experiments.

Additional experiments were conducted to demon[illegible] shrinkage as a function of restraining force and shrinkage temperature. Two oriented films having the compositions of Samples [illegible]) were prepared using a Marshall and Williams Tenter operated under typical conditions described in the Orientation section hereof. Each film thus was processed as follows:

	Sample A	Sample D
Initial Length	(22.5 inches)57.15cm	(22.5 inches)57.15cm
Stretch Length	(66 inches)168cm	(66 inches)168cm
Controlled Shrinkback Length	(60 inches)152cm	(60 inches)152 cm
Final Stabilized Length	(50 inches)127cm	50 inches)127 cm
Film Gauge (Initial)	102 microns (avg)	[illegible] microns (avg)
Film Gauge (Final)	42 microns (avg)	[illegible] microns (avg)
Draw Ratio (Initial Film Gauge/Final Film Gauge)	2.42	2.51

Strips (three for each test) of each film sample were [illegible] and subjected to shrinkage in an oven at a controlled temperature ($40^{\circ}C$ or $65.5^{\circ}C$) and at the following restraining forces: 0, 10g, [illegible] 18 g and 60 g. Each strip was permitted to shrink for [illegible] minutes. Table III presents the three-strip average for each [illegible]. These data demonstrate that the shrink [illegible]ress for the composi[illegible] of the present invention was substantially higher than the compo[illegible] of the prior art. Moreover, the shrink force for Sample [illegible]

exhibited substantially higher shrink force than the Sample [illegible] strips, even though the latter strips were substantially thicker (in gauge and hence larger cross sectional area) than the former strips.

It is preferred that the thermoplastic elastomer film of the present invention have a shrink stress of at least [illegible] g/cm² at the orientation temperature, thereby providing sufficient force for its intended purpose. It is also preferred that the shrink force at 65.5°C be at least 5,000 g/cm².

It is interesting to note from the Table III data that the shrinkage is generally linear with respect to the applied force. This permits calculating the shrink force and shrink stress. Note that the shrink temperature of 65.5°C is higher than the orientation temperature and 49°C is lower than that temperature. The higher temperature results in more shrinkage since more stresses are relieved.

Antiblock Properties

The composition of the present invention also exhibits good antiblocking properties in comparison to films of the compositions of samples D, E and F.

Multi-layers of each film Sample A, B, C, D, E and F compositions (150 micron thick unoriented) were stored for several weeks. The films were then manually separated and subjectively rated for blocking (i.e., resistance to unwinding).

Sample	Observed Blocking
A	No blocking
B	Slight tackiness
C	No blocking
D	Fully Blocked
E	Partial Blocking
F	Partial Blocking

Antiblock property is important in unwinding the film during tentering or during unwinding the oriented film of use. Sticking of the film is undesirable since it slows down the operation or renders the process inoperable.

THERMOPLASTIC ELASTOMER WITH COATING

Another embodiment of the present invention is directed specifically at solving blocking associated with thermoplastic elastomers, particularly those containing process oil and for high VA, ethylene vinyl acetate. These films are tacky by nature and require

antiblock agents such as particulate silica. The elastomer present in these blends appears to prevent uniform distribution of particulate antiblock in the resin with the result that the antiblock does not become uniformly distributed on the film surface.

In one aspect of this invention, a thin coating of an ethylene polymer or copolymer is provided on one or both sides of the base thermoplastic elastomer (core). The subsequent stretching of the film further reduces the thickness of the coating. The coating thickness ratio (final/initial) is in proportion to the draw ratio. Preferably the coating comprises conventional low density polyethylene (LDPE) having a high Melt Index (in excess of 3.0). Other ethylene polymers and copolymers that may be used as the coating include linear low density polyethylenes (LLDPE), EVA, etc. These materials should have relatively high Melt Indices (in excess of 3.0, preferably 5.0-30.0) and should be capable of high draw down, making them suitable for coextrusion with the base resin (core layer), and should possess non-tacky properties or be treatable to a nontacky condition (e.g. addition of antiblock). Coextrusion is the preferred coating method, but extrusion coating may also be used.

It is essential that the coating be sufficiently thin to avoid interference with the shrink and elastic properties of the thermoplastic elastomer but sufficiently thick to impart antiblock properties to the composite. This latter requirement means that the coating must be capable of carrying uniformly distributed therein particulate finely divided antiblock agent.

As applied to the core or base resin, the coating will comprise between 2 to 15, preferably 2 to 10 weight percent of the composite and not more than 25 microns thick. Following the orientation, the coating will be reduced to a thickness of not more than 7 microns and as thin as possible. Preferred thickness after orientation is between 1 and 5 microns.

The amount of antiblock in the coating may range from 500 to 5,000 ppm, with 1,000 to 4,000 being preferred. The coating may also include slip agents such as erucamide and oleamide.

The coating may be applied to only one side of the base resin but preferably is applied to both sides.

It should be noted that the invention comprising the coating embodiment is not restricted to the thermoplastic elastomer composition specified in the earlier description of the "Elastomer Component" as the core (although these compositions are the most preferred) but may instead contemplate the use of any thermoplastic elastomer resin composition. The preferred resin composition comprises from [illegible] 35 wt % of the elastomer component, from 35 to 80 wt % of the [illegible]nent, and from 2 to 25 wt % of the processing oil component.

OPERATION

In practice, the process of the present [illegible] may be carried out using an in-line operation wherein the extruder and orientation system (e.g., tenter) are arranged in tandem to form the film by casting or melt embossing followed by [illegible] orientation. Alternatively, these operations may be carried out [illegible]tely.

In a preferred embodiment, the compounded resin containing the three main ingredients along with the other additives is introduced into an extruder and extruded into a web from a flat or coat-hanger type die and melt embossed through counter rotating chill [illegible] and embossing rolls. The film thickness may vary from 50 to 400 microns before orientation and from 10 to 200 microns after orientation. Preferably the film will have a final stabilized thickness of between 10 and 100 microns after orientation and annealing. The film is wound on a take up roll and transferred to [illegible] equipment or processed in line with the tenter.

The edges of the film are gripped in the [illegible] and passed successively through (a) a preheat stage, (b) an [illegible] stage wherein the film is stretched laterally at an elevated [illegible], (c) an annealing stage and, finally, (d) a cooling stage where the stretched film is cooled to near ambient temperature. [illegible] restraining force is released, the film snaps back sligh[illegible] [illegible] retains most of its stretched length. This film is wound on [illegible] roll, ready for transport or use.

The dimensionally stable [illegible] may be secured [illegible] substrate and heated causing it to shrink. Shrinkage com[illegible] few degrees above storage temperature, reaching maximum at some temperature above the orientation temperature.

In the embodiment for the coating of a thermoplastic elas- mer, the operation may be the same as above except that in extrus of the resin to form the film, a coextrusion die may be used to app the thin coating on one or both sides of the thermoplastic elastom core.

In either embodiment, the film produced has excellen[illegible] force properties and good antiblock properties.

TABLE I

Component	FILM SAMPLE			COMPARATIVE FILM SAMPLES		
	A	B	C	D	E	F
Elastomer[1]	22.6 wt %	27.0 wt %	39.4 wt %	39.4 wt %	22.6 wt %	27.0 wt %
EVA[2]	71.7 wt %	66.2 wt %	55.0 wt %	41.6 wt %	58.4 wt %	49.6 wt %
Process Oil[3]	5.6 wt %	6.8 wt %	5.6 wt %	19.0 wt %	19.0 wt %	23.4 wt %
MI	3.25	2.63	2.16	2.66	6.6	10.3

1 Ethylene-propylene copolymer rubber marketed as Vistalon 3708 by Exxon Chemical Company.

2 LD-767 (28 wt % VA) sold by Exxon Chemical Company.

3 Arco Prime 350 sold by Arco Chemical Company.

16

TABLE II

Sample	Test	Initial Gauge (microns)	Initial Length (cm)	Final Length (cm)	% Recovery (Actual Draw)	Calculated Shrink Force (grams)
A	Free	157.5	8.0	4.3	91.6	
	Restrained	149.9	8.0	4.5	87.5	222
B	Free	157.5	8.0	4.4	90.0	
	Restrained	157.5	8.0	4.5	86.8	450
C	Free	152.4	8.0	4.4	89.9	
	Restrained	154.9	7.9	4.6	85.6	169
D	Free	152.4	8.1	4.3	91.9	
	Restrained	149.9	8.2	4.7	82.2	134
E	Free	160.0	7.9	4.3	91.5	
	Restrained	162.6	8.0	4.7	82.6	148
F	Free	157.18	8.1	4.4	88.5	
	Restrained	152.4	8.1	4.7	81.3	127

TABLE III

Restraining Force (grams)		Strip Length after shrinkage (cm) 0	12	24	36	48	60	Shrink Force (grams)**	Area (cm^2)	Shrink Stress g/cm^2
Sample A*	49°C	8.08	8.33	9.62	8.89	9.08	9.33	91	.010	9,100
	65.5°C	5.83	6.26	6.98	7.73	8.38	9.43	73	.011	6,636
Sample D*	49°C	8.57	8.82	9.15	9.41	9.74	10.01	59	.014	4,214
	65.5°C	5.73	6.23	6.91	7.90	8.75	10.04	65	.016	4,063

* three strip sample average

** calculated

[illegible]

1. An oriented film having a blend composition [illegible] from 5 to 40 weight percent of an olefinic elastomer, [illegible] weight percent of a normally liquid process oil, and from 50 to [illegible] percent of a thermoplastic ethylene copolymer, said [illegible] oriented in draw ratio of from 1.5 [illegible] and [illegible] [illegible]ally stable, thermally unstable in the stretch [illegible] and contractible to a thermally stable and elastic [illegible] application of heat.

2. A film as defined in claim 1 wherein the thermoplastic ethylene copolymer is EVA, EA or EMA [illegible] film has been stretch oriented in the transverse [illegible] temperature not less than 37°C and not more than 5.6°C below the crystalline melting point of the copolymer and partially annealed in stressed condition.

3. A film as defined in claim 3 wherein the blend composition comprises from 15 to 30 weight percent of EPM or EPDM as olefinic elastomer, from 60 to 80 weight percent of EVA having a vinyl acetate content of 9 to 40 weight percent, and from 2 to 10 weight percent of a normally liquid aromatic, naphthenic or paraffinic process oil.

4. A film as defined in claim 3 wherein the composition comprises from 20 to 30 weight percent of the olefinic elastomer, from 6[illegible] to 75 weight percent of the EVA, and from 4 to 8 weight percent of the processing oil.

5. [illegible] film as defined in any of claims 1 to 4, wherein the film has been stretch oriented in the transverse direction at a draw ratio of from [illegible] 2:1 to 4:1.

6. A film as defined in any of claims 1 to 5, wherein the film has a shrink stress of at least 5,000 g/cm^2 at the stretch or orientation temperature.

7. A composite comprising
(a) a first layer comprising the film defined in any of claims 1 to 6; and
(b) a second layer of stretch oriented film on said first layer and comprising a polymer or copolymer of ethylene having a Melt Index of at least 3.0, said second layer being no thicker than 7 microns in the stretched condition and comprising from 2 to 15 weight percent of the composite.

8. A composite as defined in claim 7 wherein said second layer is coextruded with said first layer.

9. A composite as defined in claim 7 or claim 8, wherein the second layer comprises LDPE having a Melt Index between 5 and 30.

10. A composite as defined in claim 9 wherein a layer of LDPE is coextruded onto each side of said first layer.

11. An oriented composite comprising
(a) a layer of a thermoplastic elastomer film containing from 2 to 25 wt % of a process oil; and
(b) a coating of a polymer or copolymer of [illegible] coextruded with said first layer and having a Melt Index of between 5 and 30, said coating being less than 7 microns thick in the oriented condition and containing from 500 to 5,000 ppm of a particulate antiblock agent.

12. A process for preparing a heat shrinkable [illegible] comprising

(a) extruding a molten blend comprising

(i) from 10 to 40 weight percent of an [illegible]

(ii) not more than 10 weight percent of a [illegible] carbon oil; and

(iii) from 50 to 80 weight percent [illegible] plastic copolymer of ethylene;

(b) stretch orienting the film in the TD [illegible] times its original length at a temperature not less than 37°C and not more than 5.6°C below the crystalline melting point of the [illegible] copolymer;

(c) partially annealing the stretched film;

(d) cooling the film while maintaining [illegible] film.

13. A process as defined in claim 12 wherein the ethylene copolymer is EVA, EAA, or EMA.

14. A process as defined in claim 13 wherein the annealing step is carried out under stress and at a temperature between ± 11.1°C of the orienting temperature.

15. A process as defined in claim 14 wherein [illegible] and cooling steps are carried out in part by permitting the [illegible] shrink in the TD by no more than 30% of the total stretch distance.

16. A process as defined in any of claims 12 to 15 wherein the stretch orientation stretches the film by from 2 to 4 times its original length in the TD.

17. A process for preparing a heat shrinka[illegible] comprises

(a) stretch orienting a film having a thickness of betw[illegible] 50 and 400 microns and a composition of

(i) from 15 to 30 weight percent of an EPM or [illegible] elastomer;

(ii) from 60 to 80 weight percent of an ethyle[illegible] acetate copolymer (EVA) having a vinyl [illegible] content of about 15 to 35 weight per[illegible]

(iii) from 2 to 10 weight percent of a normally liquid hydrocarbon process oil

by drawing the film in the transverse di[illegible] to 9 times its original length at a [illegible] 37°C to below the crystalline melting point of [illegible]

(b) partially annealing the film at an annealing [illegible] of ± 22.2°C of the stretch temperature but less th[illegible] the crystalline melting point of the EVA while maintaining a stress on the film; and

(c) cooling the film to ambient temperature while maintaining a stress on the film during at least a portion of the step.

[illegible] A process for manufacturing a heat [illegible] composite having improved antiblock properties which comprises

(a) preparing a film of from 50 to 400 micron thickness from a thermoplastic elastomer resin composition comprising an elastomer, a thermoplast[illegible] polyolefin and a processing oil;

(b) coextruding with said thermoplastic elastomer a layer of an ethylene polymer or copolymer to form a composite, said polymer or copolymer having a Melt Index of at least 3.0, and constituting up to 15 wt % of the composite and having a thickness less than 25 microns;

(c) stretch orienting the composite at a temperature not less than 57°C and not greater than ... the crystalline melting point of the ... by a draw ratio of from 1.5:1 and ... the layer thickness is no greater than ... microns; and

(d) cooling the stretched composite ... dimensionally stable elastomeric composite ... composite being heat shrinkable ... temperatures above the cooling temperatures.

19. A composite comprising

(a) a layer of flexible substantially inelastic material;

(b) a layer of film as defined in any of claims 1 to ... secured to the layer of flexible substantially inelastic material whereby application of heat contracts both the film and the layer of flexible, substantially inelastic material.

20. A process for preparing an elasticized composite material which comprises

(a) stretch orienting a film having a thickness of from 50 and 400 microns and a composition of

(i) from 15 to 30 weight percent of an EPM or ... elastomer;

(ii) from 60 to 80 weight percent of ... vinyl acetate copolymer (EVA) ... acetate content of from ... to ... cent; and

(iii) from 2 to 10 weight percent ... liquid hydrocarbon process oil;

by drawing the film in the transverse direction from 1.5 to 9 times its original length at a temperature not less than 37°C and below the crystalline melting point of the EVA;

(b) annealing the film at an annealing temperature of $\pm$ 11.1°C of the orientation temperature while maintaining a stress on the film;

(c) cooling the film to room temperature;

(d) securing a strip of the film to a layer of flexible, substantially inelastic material at longitudinally spaced locations along the film to form a composite;

(e) heating the composite to a temperature in excess of 37°C to within $\pm$ 11.1°C of the orienting temperature whereby the film and the layer of flexible, substantially inelastic material contract to an elastic heat stable condition.

21. The process of claim 19 wherein the orienting temperature and annealing temperature are between 37°C and 71°C.

22. The film of claim 3 wherein the EVA has a VA content of from 15 and 35 wt %.